PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C01B 31/02, B01J 31/02, 20/26

A1

(11) International Publication Number: WO 98/09913

(43) International Publication Date: 12 March 1998 (12.03.98)

(21) International Application Number: PCT/US96/14555

(22) International Filing Date: 6 September 1996 (06.09.96)

(71) Applicant (*for all designated States except US*): UNIVERSITY OF MASSACHUSETTS [US/US]; 55 Lake Avenue, North, Worcester, MA 01655-0243 (US).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): ROTELLO, Vincent [US/US]; 107 East Pleasant Street, Amherst, MA 01002 (US).

(74) Agents: DECONTI, Giulio, A., Jr. et al.; Lahive & Cockfield, LLP, 28 State Street, Boston, MA 02109 (US).

(81) Designated States: AU, CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: REVERSIBLE COVALENT ATTACHMENT OF FULLERENES TO INSOLUBLE SUPPORTS

(57) Abstract

Methods of separating fullerenes from a mixture by covalent attachment to an insoluble support are disclosed. Compositions useful in the method, and methods of preparing the compositions, are also described.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

REVERSIBLE COVALENT ATTACHMENT OF FULLERENES TO INSOLUBLE SUPPORTS

Background of the Invention

Fullerenes and their derivatives posses a number of potentially useful magnetic, electronic, biological, and chemical properties. Recent advances in fullerene production have made crude fullerenes available in large quantities. However, one major limit to the use of fullerenes is the high cost of purification of the different fullerenes from each other and from byproducts, such as soot, that are formed during the fullerene synthesis.

Current methodologies for the purification of fullerenes rely upon chromatographic techniques to separate the individual fullerenes and the undesired byproducts. For example, fullerenes have been purified by chromatography on columns, eluting with conventional solvents (see, e.g., Mittelbach, A. *et al.* (1992) *Angew. Chem. Int. Ed. Engl.* 31:1640; Gügel, A. and Müllen, K. (1993) J. Chromatogr. 628:23). While these methods are useful for laboratory fullerene production, they generally are slow, or have limited ability to resolve various fullerene components. Also, the capacity of such techniques is often relatively low, and is limited by the capacity of the chromatographic column employed.

Fullerenes have also been purified by association with calixarenes (see, e.g., Suzuki, T; Nakashima, K.; Shinkai, S. (1995) *Tetrahedron Lett.* 249) but this method can be expensive to use for large-scale purification.

Fullerenes have been purified by a cycle of hydrogenation and dehydrogenation to separate non-fullerene impurities (see, e.g., Shigematsu, K.; Abe, K. (1991) Japanese Patent Application Serial No. 91246509). This method requires several steps and the use of hydrogenation catalysts, which are often expensive.

Polymeric supports for covalent modification of fullerenes have also been reported (see, e.g., Guhr, K.; Greaves, M.; Rotello, V. (1994) *J. Am. Chem. Soc.* 116:5997; Nie, B. *et al.*, (1995) *Tetrahedron Lett.* 3617), but can suffer from instability of the support, which can result in contamination of the purified fullerenes.

Thus, many known purification methods are not cost-effective for large scale purification.

Summary of the Invention

The present invention relates to methods for reversibly attaching fullerenes to solid supports. The invention provides solid supports suitable for covalent attachment of fullerenes, methods for preparing solid supports suitable for covalent attachment of fullerenes, and methods for purifying fullerenes using the solid supports of the invention.

Thus, in one aspect, the invention provides a composition comprising a conjugated diene moiety covalently bonded to an insoluble support selected from the group consisting of silica, alumina, titania, and zirconia.

In another aspect, the invention provides a method for preparing a composition comprising a diene moiety covalently bonded to an insoluble support selected from the group consisting of silica, alumina, titania, and zirconia. The method comprises the step of reacting the insoluble support with a diene moiety under conditions such that the diene moiety becomes covalently bonded to the solid support, to form the composition comprising a diene moiety covalently bonded to an insoluble support.

In another aspect, the invention provides a method of preparing a composition comprising a diene moiety covalently bonded to a sol-gel silica support. The method includes the steps of providing a compound comprising a diene moiety and an orthosilicate; and hydrolyzing the orthosilicate such that a sol-gel silica support is formed to obtain the composition comprising a diene moiety covalently bonded to a silica support.

In another aspect, the invention provides a composition comprising a covalent adduct of a fullerene and an insoluble support, wherein the insoluble support is selected from the group consisting of silica, alumina, titania, and zirconia.

Brief Description of the Drawings

Figure 1 is a reaction scheme which depicts the synthesis of an exemplary insoluble support for reversible covalent attachment of fullerenes.

Figure 2 shows HPLC chromatograms of fullerene extracts before and after reversible covalent attachment to an insoluble support according to the invention.

Figure 3 is a reaction scheme showing the synthesis of a silica sol-gel support with a covalently bonded diene suitable for reversible covalent attachment of fullerenes.

Detailed Description of the Invention

As an alternative to conventional procedures, the present invention provides methods for reversible covalent attachment of fullerenes to insoluble supports. The reversible covalent attachment methods of the invention are useful, e.g., as a means of fullerene purification.

The term "fullerene" is art-recognized, and as used herein refers to all-carbon species such as C_{60}, C_{70}, C_{76}, C_{78}, C_{84}, carbon nanotubes, and the like, as well as derivatives thereof. Such derivatives can include covalent adducts (for a review, see Diederich, F and Thilgen, C. (1996) *Science* 271:317) as well as non-covalent compounds such as inclusion compounds (see, e.g., Hirsch, A. "The Chemistry of the Fullerenes" (Thieme, Stuttgart, 1994)).

In general, the invention provides insoluble supports capable of undergoing reaction with fullerenes to provide a covalent adduct between the insoluble support and the

fullerene. Such supports include solid functionalized inorganic supports such as silica (e.g., silica gel, controlled-pore glass, and the like), alumina, zirconia, titania, and the like. Other inorganic supports useful as supports, e.g., for chromatography, are contemplated for use in the invention. Other preferred insoluble supports include functionalized sol-gels, such as silicate sol-gels, e.g., as described *infra*.

The insoluble support will generally be functionalized with a functional group capable of undergoing a covalent bond-forming reaction with fullerenes. Fullerenes are known to undergo a variety of covalent bond-forming reactions (see Diederich, F and Thilgen, C., *supra*). A preferred class of covalent bond-forming reactions is cycloadditions. Cycloadditions include the Diels-Alder reaction, ene reaction, 1,3-dipolar additions, [2+2] cycloadditions, and the like (see, e.g., March, J. (1985) "Advanced Organic Chemistry," 3rd Ed., John Wiley & Sons). It is known that certain cycloaddition reactions of fullerenes are reversible under certain conditions. For example, Diels-Alder reactions of fullerenes with certain dienes are reversible, often requiring only moderate heating to trigger the retro-Diels-Alder reaction, thereby regenerating the fullerene. Thus, any cycloaddition in which a fullerene can become covalently bonded to a support, and be subsequently released from the support to regenerate the original fullerene, can find use in the present invention.

Although reference is made herein to Diels-Alder reactions, in which a diene covalently bonded to a support reacts with a fullerene to yield a covalent adduct, it will be appreciated that the principles described herein can be applied to any reversible cycloaddition with a fullerene. Thus, for example, an olefin covalently bonded to a solid support can react (e.g., thermal or by photochemical initiation, optionally in the presence of a photosensitizer) with a fullerene in a [2+2] cycloaddition to yield a covalent adduct. Cycloreversion of the adduct (e.g., by thermal or photochemical reversion) regenerates the original fullerene.

A preferred cycloaddition is the Diels-Alder reaction. Fullerenes can react as dienophiles with reactive dienes to form covalent adducts. Accordingly, any diene capable of reaction with a fullerene in a Diels-Alder reaction is contemplated for use in the invention. Such dienes are generally conjugated dienes. Any diene capable of acting as a diene in a Diels-Alder reaction may be useful in the present invention. Exemplary diene moieties include 1,3-butadienyl, furanyl, cyclopentadienyl and anthracenyl, and derivatives thereof, and the like. It will be understood, however, that other moieties capable of participating in Diels-Alder reactions, including hetero-Diels-Alder reactions and inverse electron demand Diels-Alder reactions, can be useful in the present invention. Thus, enones, diazines, and other heterocyclic or heteroatomic moieties, can be used in the place of dienes. Also, it will be appreciated that the Diels-Alder reactions described herein can, in certain embodiments, be catalyzed, e.g., with catalysts known in the art.

In one embodiment, the invention provides a composition comprising a conjugated diene moiety covalently bonded to an insoluble support selected from the group consisting of silica, alumina, titania, and zirconia. In preferred embodiments, the insoluble support is a solid silica support or a silica sol-gel support. In preferred embodiments, the conjugated diene moiety is covalently bonded to a linker moiety, as described below. In preferred embodiments, the linker moiety comprises a C2 to C12 alkylene moiety or a phenylene moiety. In preferred embodiments, the linker moiety is covalently bonded to the insoluble support through an orthosilicate moiety. In preferred embodiments, the conjugated diene moiety is selected from the group consisting of cyclopentadienyl, furanyl, and anthracenyl, and derivatives thereof. The diene moiety can be selected so that covalent attachment of a fullerene, and subsequent cleavage of the fullerene, occur under appropriate conditions. Thus, for example, a highly reactive diene will generally react with a fullerene to form a covalent adduct at a lower temperature than will a less reactive diene. Similarly, an adduct of a reactive diene and a fullerene will more readily undergo cleavage, e.g., will be cleaved at a lower temperature. One of ordinary skill in the art will be able to select appropriate dienes with no more than routine experimentation.

The diene moiety can be provided with a linker moiety for covalently bonding the diene moiety to the support. Alternatively, the support can be modified with a linker moiety for attachment to the diene. The linker moiety serves to functionalize the support or the diene moiety for covalent linkage, and provides a spacer unit. For example, the propylene linker of modified silica gel **2** joins the cyclopentadienyl functionality (through a carbon-carbon bond) to the silica support (through an orthosilicate functionality). The choice of an appropriate linking moiety for a selected support and diene moiety will be routine to the skilled artisan. In certain embodiments, linking moieties can be chosen to be selectively cleavable (e.g., a linking moiety containing an ester functionality can be cleaved by hydrolysis). Non-limiting examples of linkers include C2 to C12 alkylene moieties, or phenylene, e.g., p-phenylene, moieties.

In another aspect, the invention provides a method for preparing a composition comprising a diene moiety covalently bonded to an insoluble support selected from the group consisting of silica, alumina, titania, and zirconia. The method comprises reacting the insoluble support with a diene-containing moiety under conditions such that the diene moiety becomes covalently bonded to the solid support, to form the composition comprising a diene moiety covalently bonded to an insoluble support. It will be understood that the support can be functionalized with a moiety which does not contain a diene group, but which can be converted to a diene group by suitable manipulations. In preferred embodiments, the insoluble support is a silica support. In preferred embodiments, the method comprises, prior to the reacting step, the step of reacting the insoluble support with a linker moiety under conditions such that the linker moiety becomes covalently bonded to the insoluble support.

A covalently-bonded composition comprising a support and a diene moiety, joined by a linking moiety, can be prepared by reacting a support with a linking reagent such that the linking reagent is covalently bonded to the support, followed by reaction with a diene-containing reagent to provide a diene moiety covalently bonded to the linking moiety. As shown in Figure 1, the linking moiety, when bound to the support, can include an electrophilic moiety (e.g., an alkyl halide, alkyl tosylate, enone, epoxide, ketone, acid chloride, or the like) for reaction with a nucleophile (e.g., a carbanion, amine, thiol, hydroxyl, or the like) to form a covalent bond. The choice of reactive functionalities will be routine for the ordinarily skilled artisan. Alternatively, the linking moiety can be covalently joined to the diene moiety, and the linking moiety then covalently bonded to the support.

In another embodiment, the invention provides a method for preparing a composition comprising a diene moiety covalently bonded to a sol-gel silica support. The the method comprises the steps of providing a compound comprising a diene moiety and an orthosilicate; and hydrolyzing the orthosilicate such that a sol-gel silica support is formed, to form the composition comprising a diene moiety covalently bonded to a silica support. In preferred embodiments, the hydrolyzing step comprises treating the orthosilicate with acid. This process is described in more detail in Example 3, *infra*. The sol-gel supports formed according to the methods of the invention can be provided as surfaces, or as discrete particles and can be cast or formed, as is known in the art. The sol-gel supports of the invention can provided greater porosity than other supports, and therefore can have greater accessibility to fullerene species and higher capacity for covalent attachment of fullerenes.

It has been found that dienes covalently bonded to insoluble supports such as silica have advantages compared to similar dienes covalently bonded to polymeric (e.g., resin) supports. The silica supports of the invention provide improved stability compared to polymeric supports (see, e.g., Nie, B. and Rotello, V. (1996) *J. Org. Chem.* 61:1870). The silica-based supports can be re-used repeatedly (i.e., repeated cycles of fullerene attachment and regeneration are possible without sugnificant loss of support capacity or activity toward fullerenes). In contrast, polymeric supports can degrade with repeated use, and degradation products can contaminate the fullerenes, making purification difficult. Also, the silica-based support **2** releases the fullerene at lower temperature than the resin-based polymeric supports. Without being bound by any theory, it is believed that the difference in release temperature is due, at least in part, to interactions between the polymeric resin and the immobilized diene and/or fullerene. Such interactions are decreased or absent in the silica-based support.

The diene-containing supports of the invention can be used to separate fullerenes from mixtures. For example, fullerenes can be separated from byproducts of fullerene synthesis, such as soot, as described in Example 2, *infra*. Furthermore, different fullerene

species can be separated from other fullerenes. For example, C_{60} and C_{70} can be separated from each other with the compositions of the invention, as described below.

Thus, in one aspect, the invention provides a method for separating, e.g., purifying, fullerenes from a mixture, e.g., from a reaction mixture, e.g., a mixture formed by the synthesis of fullerenes or fullerene derivatives. A mixture can include, for example, any fullerene and either a non-fullerene material or a different fullerene. The methods of the invention can be used to selectively purify mixtures of two or more fullerenes to obtain a purified fullerene or a mixture enriched in a particular fullerene. In general, the method includes contacting the mixture with a diene moiety covalently bonded to an insoluble support, under conditions such that the fullerene becomes covalently bound to the insoluble support. The insoluble support is then separated from at least a portion of the mixture. Finally, the fullerene is cleaved from the solid support so that the fullerene is separated from the mixture.

In preferred embodiments, the insoluble support is selected from the group consisting of silica, alumina, titania, and zirconia. Silica sol-gel supports are also preferred insoluble supports.

As shown in Example 1, infra, conditions for attaching fullerenes to the support can be very mild. For example, C_{60} rapidly undergoes a Diels-Alder reaction with the support 2 (Figure 1) at room temperature in toluene. In general, the conditions will be selected so that covalent bonding of the fullerene to the support occurs readily, preferably under conditions where the fullerene is not cleaved from the support at a significant rate. The conditions can include the use of a solvent, to suspend the support and suspend or dissolve the fullerene. Inert solvents are preferred, and inert aromatic solvents such as benzene, toluene, and the like are particularly preferred. In certain embodiments, the covalent bond-forming reaction can be conducted under an inert atmosphere such as nitrogen or argon gas. In preferred embodiments, the conditions for attaching fullerenes to the support include reaction temperature less than about 100°C, more preferably less than 50°C, and more preferably less than 30°C. Conditions suitable for covalent attachment of fullerenes to the support will be selected according to the fullerene and the support, and selection of such conditions will be routine to one of ordinary skill in the art.

The insoluble support can be separated from at least a portion of the mixture by methods known in the art. For example, the insoluble support, bearing the covalently-attached fullerene, can be filtered, e.g., with filter paper, a membrane, a frit, or the like, to remove solvent and soluble components of the mixture. The separated support can be washed or otherwise freed of excess solvent or impurities, and can then be suspended in fresh solvent for cleavage of the fullerenes from the support. Alternatively, the support can be treated to cleave the fullerenes without use of solvent. For example, the isolated fullerene-bearing support can be heated to cleave the covalently-bonded fullerenes (e.g.,

through a retro-Diels-Alder reaction), and the fullerenes can be isolated by sublimation without solvent.

The fullerenes are preferably cleaved from the support under conditions suitable to effect fullerene cleavage without degrading the fullerenes. It will be appreciated that conditions suitable for cleavage of fullerenes to the support will be selected according to the fullerene and the support, and selection of such conditions will be routine to one of ordinary skill in the art. For example, a covalent adduct of a fullerene with a solid support can be cleaved by heating of the support containing the adduct. For example, fullerene-containing support **3a** undergoes retro-Diels-Alder reaction at about 100°C. In preferred embodiments, the fullerene (or fullerenes) is cleaved by heating to a temperature of less than about 200°C, more preferably less than about 150°C, and still more preferably less than about 100°C. A preferred range of temperatures is from about 20°C to about 150°C. The cleavage reaction can be performed with or without a solvent, optionally under an inert atmosphere. It will be appreciated that different fullerenes can be differentially cleaved from a support. This differential release permits the selective cleavage of one fullerene from the support in the presence of another fullerene, thus providing selective separation of the fullerenes, as shown in Example 1, *infra*. Thus, for example, heating of an adduct of a mixture of fullerenes with a solid support can result in release of one fullerene at a lower temperature, followed by release of another fullerene at a higher temperature.

In one embodiment, the separation process can be carried out in a single vessel, e.g., a column, e.g., a chromatographic column. In this embodiment, the fullerenes can be cleaved from the solid support by heating the column or the eluting solvent; or, the process can be performed at a temperature such that the formation and cleavage of the fullerene:diene compound both occur in an equilibrium process. In this embodiment, the covalent adduct of the fullerene and the support need not be isolated; formation, separation, and cleavage of the adduct occur simultaneously. In certain embodiments, the contacting step comprises loading the mixture onto a column, and the separating step comprises eluting the portion of the mixture from the column.

In another aspect, the invention provides a composition comprising a covalent adduct of a fullerene and an insoluble support, wherein the insoluble support is selected from the group consisting of silica, alumina, titania, and zirconia. In certain preferred embodiments, the insoluble support is a silica sol-gel. The fullerene will generally be covalently bound through an adduct of the fullerene and a diene moiety covalent bonded to the solid support.

The invention is further illustrated by the following non-limiting examples.

Example 1

Reaction of chloropropyl-functionalized silica gel **1** (for preparation, see, e.g., Deschler, U., Kleinschmit, P. and Panster, P. (1986) *Angew. Chem. Int. Ed. Engl.* 25:236) with lithium cyclopentadienylide provided the cyclopentadiene-functionalized silica gel **2** (Figure 1). This material reacted rapidly with C_{60} at room temperature to yield a fullerene-substituted solid support (**3a**). Chloropropyl-functionalized silica gel **1**, in contrast, does not absorb C_{60}, ruling out adsorption as the means of C_{60} uptake. Similarly, benzyl ether-substituted silica gel (produced via the reaction of the sodium salt of benzyl alcohol with chloropropyl-functionalized silica gel **1**) was unreactive toward C_{60}. Maximal uptake of C_{60} by silica gel **2** was 28 mg of C_{60}/g of silica gel (7.5% of the theoretical maximum). Without wishing to be bound by any theory, it is believed that certain of the cyclopentadiene functionalities of silica gel **2** are sterically inaccessible to the bulky fullerene.

Functionalized silica gel **2** was reacted with C_{60}/C_{70} mixtures in similar fashion to provide a mixed fullerene-functionalized material (**3b**). The initial rate of C_{70} uptake by silica gel **2** was essentially the same as that observed for C_{60} (k_{C60}/k_{C70} = 1.03).

The addition of fullerenes to functionalized silica gel **2** is readily reversible and selective for C_{60}: heating of the mixed fullerene-functionalized material in toluene to 100°C for 5 h releases 93.7% of the bound C_{60} and 41.1% of the bound C_{70} (Figure 1). The release process was fully reproducible, and the fullerenes were completely reabsorbed (i.e., covalently attached to the functionalized silica gel) upon cooling of the solution. The difference in release provides fullerenes significantly enriched in C_{60}: the initial C_{60}/C_{70} ratio was 90:10, the final ratio was 96:4. This selectivity is comparable to that observed from a single iteration of the calixarene-based C_{60} purification strategy.

Example 2

With reversible binding of C_{60} and C_{70} established, the application of the reversible covalent attachment of fullerenes to the purification of fullerenes from other materials was examined. For these studies, soot extract from the potentially commercially efficient flame synthesis of fullerenes was used (see, e.g., Howard *et al.* (1991) *Nature* 352:139)). Crude soot extract in toluene (Figure 2, trace a) was reacted with functionalized silica gel **2**. The fullerene-containing silica was washed and resuspended in toluene. Heating of this solution to 100°C followed by decanting then provided purified fullerene solution, free from non-fulleroid materials (Figure 2, trace b).

In summary, we have demonstrated the reversible attachment of fullerenes to a cyclopentadiene-functionalized silica support. This process has been used to selectively extract fullerenes from extracts of fullerene-containing soot. This material also provides a means of separating individual fullerene species through selective release of C_{60}. These

diene-based materials can be used both to purify C_{60} and C_{70} from other polycyclic aromatics and to provide separation of these individual fullerene species.

Example 3

A functionalized silicate sol-gel support is made according to the following procedure, depicted in Figure 3. (3-chloropropyl)trimethoxysilane **4** (aldrich Chemical Co., Milwaukee, WI) is reacted with lithium cyclopentadienylide **5** to yield the (3-cyclopentadienylpropyl)trimethoxysilane **6**. This orthosilicate is hydrolyzed, e.g., in the presence of aqueous acid to intermediate **7**, followed by polycondensation to form a sol-gel **8**, which can be aged to complete the polymerization, and dried to remove excess solvent. For a review of sol-gel technology, see Hench, L.; West, J. (1990) *Chem. Rev.* 90:33.

Experimental Section

Lithium Cyclopentadienylide. Dicyclopentadiene (6.2 mL, 75 mmol) was heated under argon. Cyclopentadiene was distilled and collected and then added to a flask containing hexane (120 mL) and a stir bar. n-Butyllithium (47.2 mL of a 1.6 M solution in hexanes, 75 mmol) was then added to the resulting solution at room temperature, providing a white inhomogeneous mixture. The mixture was stirred at room temperature for 2 h and then filtered through a cannula under vacuum, yielding a white solid. The product was washed with hexane (2 x 100 mL) and then dried under vacuum to provide lithium cyclopentadienylide (4.98 g, 92%) as a white solid.

Cyclopentadiene-Substituted Silica Gel 2. 3-Chloropropyl-functionalized silica gel **1** (1.00 g) (C, 3.47; H, 0.82; Cl, 2.28, chloride functionalization of 0.64 mmol/g of silica gel **1**) was added in one portion to a solution of lithium cyclopentadienylide (720.4 mg, 10 mmol) in THF (100 mL) at room temperature under Ar. The suspension was stirred at 23°C for 24h, filtered and washed with THF (200 mL) to give 1.21g of a light yellow powder. Elemental analysis of cyclopentadiene-functionalized silica gel **2**: C, 5.68; H, 1.41; Cl, 2.21. When calculated for C_5H_5 content, this indicates 0.37 mmol/g, or 57% substitution.

C_{60} Functionalized Silica Gel. Cyclopentadiene-functionalized silica gel **2** (0.200 g) was added to a solution of C_{60} in toluene (10 mL, 1.39 mM). The mixture was gently shaken at room temperature for 24h, then filtered, and washed with toluene (20mL) to provide 206 mg of C_{60} functionalized silica gel as a brown solid. Elemental analysis of C_{60} functionalized silica gel: C, 7.69; H, 1.38, indicating 0.028 mmol of C_{60}/g of C_{60} functionalized silica gel, equivalent to about 20.1 mg C_{60}/g of C_{60} functionalized silica gel.

Mixed C_{60}/C_{70} Functionalized Silica Gel. Cyclopentadiene-functionalized silica gel **2** (100 mg) was added to an extract of fullerene-containing soot (MER, Tuscon, AZ) in toluene (initial concentrations C_{60}, 1.283 mM, C_{70}, 0.136 mM). The mixture was gently

shaken at room temperature for 3.5 h, then filtered, and washed with toluene (20mL) to provide 102 mg of the mixed C_{60}/C_{70} functionalized silica gel.

Kinetics Measurements. Fullerene uptake was determined via HPLC, using a reversed-phase C18 column (Rainin Instruments, Woburn, MA). The fullerenes were eluted using a 70:30 methylene chloride/acentonitrile solvent system and were detected at 265 nm, using pyrene as an internal standard.

HPLC Assay of Soot Purification. Cyclopentadiene-functionalized silica gel **2** (100 mg) was added to an extract of flame-synthesized soot in toluene (5 mL) (initial concentrations C_{60}, 0.201 mM, C_{70}, 0.124 mM). The mixture was gently shaken for 1 h, and the liquid phase was assayed by HPLC using a 0-99% methanol/methylene chloride gradient. The silica gel was then filtered and repeatedly washed with toluene (100 mL). A portion of this silica gel (65 mg) from above was heated in toluene (2.5 mL) at 100°C under argon for 1 h, and the liquid phase was assayed by HPLC.

The contents of all references described herein are hereby incorporated by reference.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents are considered to be within the scope of this invention and are covered by the following claims.

CLAIMS

1. A composition comprising a conjugated diene moiety covalently bonded to an insoluble support selected from the group consisting of silica, alumina, titania, and zirconia.

2. The composition of claim 1, wherein the insoluble support is a solid silica support.

3. The composition of claim 1, wherein the insoluble support is a silica sol-gel support.

4. The composition of claim 1, wherein the conjugated diene moiety is covalently bonded to a linker moiety.

5. The composition of claim 4, wherein the linker moiety comprises a C2 to C12 alkylene moiety or a phenylene moiety.

6. The composition of claim 4, wherein the linker moiety is covalently bonded to the insoluble support through an orthosilicate moiety.

7. The composition of claim 1, wherein the conjugated diene moiety is selected from the group consisting of cyclopentadienyl, furanyl, and anthracenyl.

8. A method for preparing a composition comprising a diene moiety covalently bonded to an insoluble support selected from the group consisting of silica, alumina, titania, and zirconia, the method comprising the step of:

reacting the insoluble support with a diene moiety under conditions such that the diene moiety becomes covalently bonded to the solid support, to form the composition comprising a diene moiety covalently bonded to an insoluble support.

9. The method of claim 8, wherein the insoluble support is a silica support.

10. The method of claim 9, wherein the method comprises, prior to the reacting step, the step of reacting the insoluble support with a linker moiety under conditions such that the linker moiety becomes covalently bonded to the insoluble support.

11. A method of preparing a composition comprising a diene moiety covalently bonded to a sol-gel silica support, the method comprising the steps of:

providing a compound comprising a diene moiety and an orthosilicate; and

hydrolyzing the orthosilicate such that a sol-gel silica support is formed to obtain the composition comprising a diene moiety covalently bonded to a silica support.

12. The method of claim 11, wherein the hydrolyzing step comprises treating the orthosilicate with acid.

13. A method for separating a fullerene from a mixture, the method comprising the steps of:

contacting the mixture with a diene moiety covalently bonded to an insoluble support selected from the group consisting of silica, alumina, titania, and zirconia, under conditions such that the fullerene becomes covalently bound to the insoluble support;

separating the insoluble support from a portion of the mixture; and

cleaving the fullerene from the solid support to obtain the fullerene separated from the mixture.

14. The method of claim 13, wherein the fullerene undergoes a cycloaddition reaction with the diene moiety.

15. The method of claim 13, wherein the cleaving step comprises heating the insoluble support.

16. The method of claim 15, wherein the insoluble support is heated to a temperature of 25°C to 150°C.

17. The method of claim 13, wherein the separating step comprises filtering the mixture.

18. The method of claim 13, wherein the contacting step comprises loading the mixture onto a column, and the separating step comprises eluting the portion of the mixture from the column.

19. A composition comprising a covalent adduct of a fullerene and an insoluble support, wherein the insoluble support is selected from the group consisting of silica, alumina, titania, and zirconia.

20. The composition of claim 19, wherein the insoluble support is a silica sol-gel.

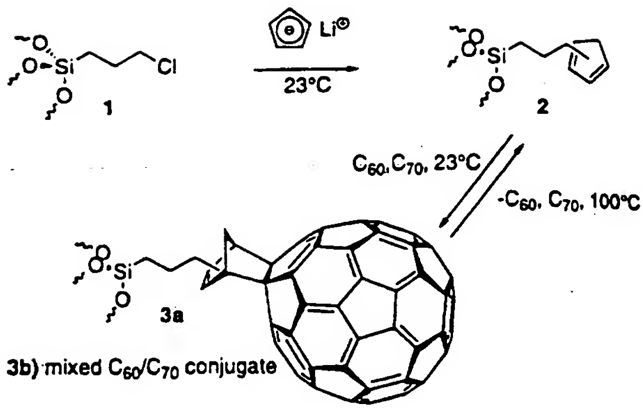
Li⊕
23°C
1
2
C_{60}, C_{70}, 23°C
-C_{60}, C_{70}, 100°C
3a
3b) mixed C_{60}/C_{70} conjugate

FIGURE 1

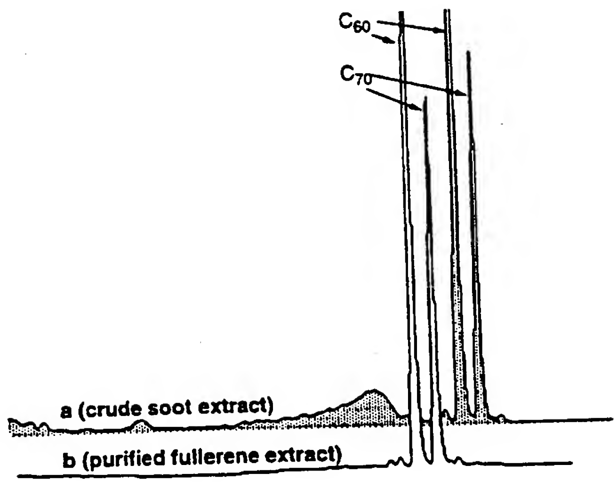

FIGURE 2

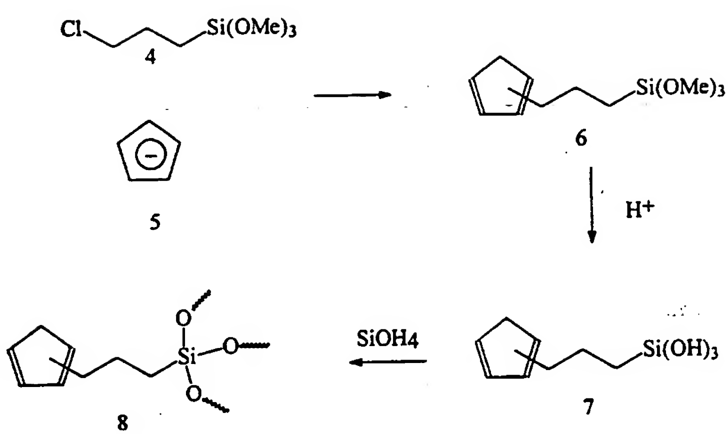

FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/14555

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :CO1B 31/02; B01J 31/02, 20/26
US CL :423/461, 445B; 502/150, 151, 402, 405
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/461, 445B; 502/150, 151, 402, 405

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: fullerenes, cycloaddition , supported diene

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,308,481 A (STALLING ET AL) 3 May 1994 (03/05/94), see entire document.	1-20
Y	US 5,580,697 A (KEANA ET AL) 3 December 1996 (03/12/96), see entire document, especially column 25, line 50-60.	1-7
Y	US 5,281,406 A (STALLING ET AL) 25 January 1994 (25/01/94), see entire document especially column 7, line 35-68.	1-7
Y	US 5,487,831 A (PIRKLE ET AL) 30 January 1996 (30/01/96), see entire docmument.	1-20
Y,E	US 5,582,955 A (KEANA ET AL) 10 December 1996 (10/12/96), see entire document.	1-20

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date		
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search 03 FEBRUARY 1997	Date of mailing of the international search report 19 FEB 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer NADINE PREISCH Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,338,571 ~~A~~ (MIRKIN ET AL) 16 August 1994 (16/08/94), see entire document.	1-20